

California Environmental Protection Agency



Air Resources Board

Trichloronitromethane (Chloropicrin) Analytical Results for Agricultural Application Air Monitoring Samples

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1.0 INTRODUCTION

The Department of Pesticide Regulation (DPR) requested the Air Resources Board (ARB) to conduct application air monitoring for trichloronitromethane (chloropicrin). This report covers the analytical and quality assurance results for a chloropicrin agricultural application occurring over a four (4) day period in Santa Barbara County. DPR requested a method estimated quantitation limit (EQL) of 0.1 microgram per cubic meter ($\mu\text{g}/\text{m}^3$). The analytical EQL achieved during this project was 0.1 $\mu\text{g}/\text{m}^3$.

2.0 METHOD DEVELOPMENT

2.1 Overview

XAD-4 cartridges are used for application air sampling. After sampling, cartridges are stored at or below four (4) degrees centigrade before extraction. Sample cartridges are extracted with three (3) milliliters of methylene chloride and desorbed in an ultrasonic bath. Sample extracts are analyzed using a gas chromatograph/mass selective detector which is operated in the selected ion-monitoring mode. Sample analysis and quantitation used the external standard method. The estimated quantitation level for this method, based on 0.144 cubic meters (m^3) of air collected, and a final extract volume of three (3) ml, is 0.1 $\mu\text{g}/\text{m}^3$.

2.2 Calibration Curve

Laboratory staff used standard concentrations of approximately 5, 10, 22, 52, 150, and 310 ng/ml to produce a six (6) point calibration curve. All calibration curves performed had a r^2 (coefficient of determination) greater than or equal to 0.995. Laboratory staff performed calibrations at the beginning of the monitoring program, after instrument maintenance, after remaking of external standard, and whenever the continuing calibration verification standard (CCV) did not fall within +/- 20 percent (%) of the expected value.

2.3 Method Detection Limit (MDL)

The MDL calculation follows the United States Environmental Protection Agency procedures for calculating MDL's. Using the analysis of seven low-level matrix spikes (5.0 ng/ml), the MDL and EQL for a three (3) ml extract is calculated as follows:

*s = the standard deviation of the concentration calculated for the seven replicate spikes.
For Chloropicrin: $s = 0.3057$ ng/ml*

$$MDL = (3.14) \times (s) = (3.14) \times (0.3057) = 0.96 \text{ ng/ml.}$$

$$EQL = (5) \times (MDL) = (5) \times (0.96) = 4.78 \text{ ng/ml}$$

$$EQL \text{ for total ng/sample} = 14.35 \text{ ng/sample}^*$$

** assuming a 3 ml final extract volume*

Based on a total collection volume of 0.144 m^3 the EQL would be $0.1 \mu\text{g}/\text{m}^3$. Staff report results above the EQL to three (3) significant figures. Results below the EQL but greater than or equal to the MDL are reported as detected (DET). Results less than MDL are reported as <MDL.

2.4 Method Development

Instrument reproducibility, collection and extraction efficiency, storage stability and breakthrough studies were performed and reported in the document "Air Sampling Cartridge Method Development and Analysis Results for Application Monitoring of Trichloronitromethane (Chloropicrin)", 2002. No additional method development was required for this application project.

3.0 CHLOROPICRIN APPLICATION AIR MONITORING SAMPLE RESULTS.

The laboratory received 62 application samples plus eight (8) field spikes, four (4) trip blanks, and four (4) trip spikes on October 22, 2005. Table 1 presents the results of the analysis of the chloropicrin agricultural application air samples by sampler location.

4.0 ANALYTICAL QUALITY CONTROL SAMPLES

4.1 System Blanks

Laboratory staff analyzes a system blank with each analytical batch, after each CCV, after every tenth sample and after samples containing high levels of chloropicrin or co-extracted contaminants. Staff defines the analytical batch as all the samples extracted together, but not to exceed twenty (20) samples. The system blank is run to insure the solvent and instrument do not contribute interferences to the analysis, and to minimize carryover from high level samples. All system blanks were less than the MDL.

4.2 Method Blanks

Laboratory staff analyzed a method blank with each analytical batch. This is an XAD-4 cartridge prepared and analyzed as described for the application samples. Laboratory staff analyzed eight (8) method blanks during this project. All method blank results were less than the MDL.

4.3 Laboratory Control Samples (LCS)

Laboratory staff analyzed a LCS with each analytical batch. A LCS is an XAD-4 cartridge spiked with 300 ng of chloropicrin. The LCS was prepared from a different stock standard than was used for the calibration standards. The LCS is extracted and analyzed as described for the samples. The LCS recoveries averaged 92.87% with a standard deviation of 5.60%.

4.4 Continuing Calibration Verification Standards (CCV)

Following standard lab procedures, laboratory staff analyzed a CCV after every calibration curve, after every tenth (10) sample and at the end of an analytical batch. The CCV must be within +/- 20% of the expected value. If any of the CCVs are outside this limit, the affected samples data is evaluated and may result in re-analysis of the affected batch. The CCV target value for this project was 22 ng/ml. All CCV's were within +/- 20 % of the expected value except those CCV's run with the initial background and field spike samples. These samples were rerun and all CCV's were within acceptable limits.

4.5 Laboratory Duplicates

No laboratory duplicates were run with this project.

5.0 FIELD, TRIP, AND LABORATORY SPIKES AND TRIP BLANKS

During the agricultural application project, four (4) trip and eight (8) field spikes along with four (4) laboratory spikes and four (4) trip blanks were analyzed. Laboratory staff prepared all spikes at 300 ng/sample of chloropicrin

5.1 Laboratory Spikes

Table 2 presents the results of the laboratory spikes. The average chloropicrin recovery was 99.19% with a standard deviation of 4.43%.

5.2 Trip Spikes

Table 2 presents the results of the trip spikes. The average chloropicrin recovery was 100.72 % with a standard deviation of 2.32%.

5.3 Field Spikes

Eight field spikes were analyzed during this application study. The range of chloropicrin detected was 373 to 708 ng/sample. The eight (8) collocated non-spiked samples had chloropicrin results ranging from 87 to 411 ng/sample. The field spike samples were spiked with 300 ng/sample. After subtracting the background results the average field spike recovery was 94.72 with a standard deviation of 6.50%. The corrected sample

results are given in Table 2.

5.4 *Trip Blanks*

Table 2 presents the results of the trip blanks. Four (4) trip blanks, with result less than the MDL, were received during this project.

6.0 DISCUSSION

During the project, 62 application samples were analyzed. Sixty-two (62) samples had results greater than the EQL of 14.4 ng/sample. The concentrations ranged from 17.88 to 20791 ng/sample.

After initial analysis, 34 samples had results above the high calibration point. These samples were diluted and the results reported in Table 1. In addition to the analysis of the front cartridge section, the back sections of samples with log numbers 22, 23, 24 and 25 were analyzed to evaluate potential analyte breakthrough. The range of concentrations for the initial analyses was 9488 to 20791 ng/sample. All back section results were less than the MDL. Consequently, no other back sections were analyzed.

LCS spiked at 300 ng/sample and processed in the same way as field samples had recoveries that averaged 92.87% with a standard deviation of 5.60%. Based on three (3) standard deviations from the mean, the acceptable recovery range was 76.07% to 109.67%. All LCS results fell within this range.

Continuing calibration verification (CCV) standard recoveries during the initial background and field spike analyses were outside the +/- 20% control limits. These samples were reanalyzed with a new CCV standard and all recoveries were within the acceptable control limits. Staff believes the original CCV was bad, but the original sample results were correct. The original sample analyses were reported.

Field spike NE-C-B-FS had a recovery much lower than the other field spikes. During the reanalysis of the field spikes this trend repeated. There were no anomalous events during the extraction and analysis to explain this lower recovery.

**Table 1: Agricultural Application Air Monitoring Results
for Chloropicrin**

Site	Log Number	Date Received	Sample ID	Date Analyzed	Chloropicrin amount (ug/sample)
E	22B	10/22/05	E-C-1	11/14/05	<MDL
	22	10/22/05	E-C-1	11/8/05	1.54E+01
	31	10/22/05	E-C-2	11/8/05	7.44E+00
	40	10/22/05	E-C-3	11/8/05	5.54E+00
	49	10/22/05	E-C-4	11/9/05	1.97E+00
	58	10/22/05	E-C-5	11/10/05	4.31E+00
	67	10/22/05	E-C-6	11/9/05	1.94E+00
N	20	10/22/05	N-C-1	10/28/05	2.52E-01
	29	10/22/05	N-C-2	11/8/05	5.65E+00
	38	10/22/05	N-C-3	11/1/05	7.78E-01
	47	10/22/05	N-C-4	11/9/05	5.16E+00
	56	10/22/05	N-C-5	11/4/05	4.93E-01
	65	10/22/05	N-C-6	11/9/05	1.36E+00
NE	5	10/22/05	NE-C-B-S	10/26/05	2.60E-01
	13	10/22/05	NE-C-B1-S	10/27/05	3.62E-01
	21	10/22/05	NE-C-1	11/8/05	1.32E+00
	30	10/22/05	NE-C-2	11/8/05	1.28E+00
	39	10/22/05	NE-C-3	11/1/05	8.04E-01
	48	10/22/05	NE-C-4	11/9/05	9.71E-01
	57	10/22/05	NE-C-5	11/4/05	1.76E-01
	66	10/22/05	NE-C-6	11/9/05	1.08E+00
NW	3	10/22/05	NW-C-B-S	10/26/05	9.26E-02
	11	10/22/05	NW-C-B1-S	10/27/05	8.86E-02
	19	10/22/05	NW-C-1	10/28/05	2.01E-02
	28	10/22/05	NW-C-2	11/8/05	2.74E+00
	37	10/22/05	NW-C-3	11/1/05	8.77E-01
	46	10/22/05	NW-C-4	11/9/05	3.05E+00
	55	10/22/05	NW-C-5	11/4/05	7.66E-01
	64	10/22/05	NW-C-6	11/7/05	3.42E-01

**Table 1: Agricultural Application Air Monitoring Results
for Chloropicrin**

Site	Log Number	Date Received	Sample ID	Date Analyzed	Chloropicrin amount (ug/sample)
S	25B	10/22/05	S-C-1	11/14/05	<MDL
	25	10/22/05	S-C-1	11/8/05	9.49E+00
	34	10/22/05	S-C-2	11/8/05	4.94E+00
	43	10/22/05	S-C-3	11/9/05	3.81E+00
	52	10/22/05	S-C-4	11/3/05	6.61E-01
	61	10/22/05	S-C-5	11/10/05	2.75E+00
	70	10/22/05	S-C-6	11/7/05	8.44E-01
SE	7	10/22/05	SE-C-B-S	10/26/05	9.20E-02
	15	10/22/05	SE-C-B1-S	10/27/05	4.12E-01
	23B	10/22/05	SE-C-1	11/14/05	<MDL
	23	10/22/05	SE-C-1	11/8/05	2.05E+01
	24B	10/22/05	SE-C-1-C	11/14/05	<MDL
	24	10/22/05	SE-C-1-C	11/8/05	2.08E+01
	32	10/22/05	SE-C-2	11/8/05	8.14E+00
	33	10/22/05	SE-C-2-C	11/8/05	7.33E+00
	41	10/22/05	SE-C-3	11/8/05	5.60E+00
	42	10/22/05	SE-C-3-C	11/8/05	5.22E+00
	50	10/22/05	SE-C-4	11/9/05	1.05E+00
	51	10/22/05	SE-C-4-C	11/9/05	9.58E-01
	59	10/22/05	SE-C-5	11/10/05	5.78E+00
	60	10/22/05	SE-C-5-C	11/10/05	5.94E+00
	68	10/22/05	SE-C-6	11/10/05	1.45E+00
	69	10/22/05	SE-C-6-C	11/10/05	1.33E+00
SW	1	10/22/05	SW-C-B-S	10/26/05	1.57E-01
	9	10/22/05	SW-C-B1-S	10/27/05	8.73E-02
	17	10/22/05	SW-C-1	10/28/05	4.65E-02
	26	10/22/05	SW-C-2	10/31/05	5.25E-01
	35	10/22/05	SW-C-3	11/1/05	8.55E-01
	44	10/22/05	SW-C-4	11/3/05	2.45E-01
	53	10/22/05	SW-C-5	11/4/05	1.01E-01
	62	10/22/05	SW-C-6	11/7/05	2.21E-01

**Table 1: Agricultural Application Air Monitoring Results
for Chloropicrin**

Site	Log Number	Date Received	Sample ID	Date Analyzed	Chloropicrin amount (ug/sample)
W	18	10/22/05	W-C-1	10/28/05	1.79E-02
	27	10/22/05	W-C-2	11/8/05	1.92E+00
	36	10/22/05	W-C-3	11/8/05	1.22E+00
	45	10/22/05	W-C-4	11/9/05	1.88E+00
	54	10/22/05	W-C-5	11/4/05	5.35E-01
	63	10/22/05	W-C-6	11/7/05	3.25E-01

Notes:

If analytical result is \geq MDL and $<$ EQL it is reported in the table as detected (DET). Levels at or above the EQL are reported as the actual measured value and are reported to three significant figures.

ug = microgram

Sample Log Numbers followed with the letter B are the cartridge back section results for the corresponding cartridge front section, log number without the B.

Sample ID (Sample identification) numbers followed by the letter C are collocated samples for the samples with the corresponding number.

Sample ID numbers including a B or B1 are background samples collected prior to chloropicrin application.

Results used from a sample dilution are reported in bold type

Site location identification:

E: East
 N: North
 NE: Northeast
 NW: Northwest
 S: South
 SE: Southeast
 SW: Southwest
 W: West

Table 2: Field QC Sample Results
Chloropicrin Application

Quality Control Type	Log Number	Laboratory ID	Date Analyzed	Chloropicrin amount (ng/sample)	Percent Recovery ¹
Lab Spike (300 ng)		LS1026A	10/26/05	301.77	100.59
		LS1026B	10/26/05	314.46	104.82
		LS1027A	10/27/05	288.36	96.12
		LS1027B	10/27/05	285.69	95.23

Field Spike (300 ng)	2	SW-C-B-FS	10/26/05	437.34	93.48
	10	SW-C-B1-FS	10/27/05	389.28	100.65
	8	SE-C-B-FS	10/26/05	382.20	96.75
	16	SE-C-B1-FS	10/27/05	708.15	98.88
	4	NW-C-B-FS	10/26/05	386.13	97.83
	12	NW-C-B1-FS	10/27/05	373.50	94.98
	6	NE-C-B-FS	10/26/05	499.35	79.65
	14	NE-C-B1-FS	10/27/05	648.54	95.57

Trip Spike (300 ng)	71	TS1026a	10/26/05	295.26	98.42
	72	TS1026b	10/26/05	303.63	101.21
	73	TS1026c	10/26/05	311.25	103.75
	74	TS1026d	10/26/05	298.50	99.50

Trip Blank	75	TB1027a	10/27/05	ND	<MDL
	76	TB1027b	10/27/05	ND	<MDL
	77	TB1027c	10/27/05	ND	<MDL
	78	TB1027d	10/27/05	ND	<MDL

Notes:

* Field spike values are not corrected for background levels.

ID Identification

<MDL Less than method detection limit

ng Nanograms

1 Value after collocated background result subtracted